

REMARKS:

Claims 1, 2, and 4-21 are pending. Claim 3 has been cancelled. Claims 1, 2, 4-9 have been amended to correct for formalities including antecedent basis and grammatical and typographical errors. Support for amended claim 1 is found, *inter alia*, in the specification starting on page 12, line 11, to page 13, line 20. Support for amended claim 4 is found, *inter alia*, in the specification on page 3, lines 10-16. Support for amended claim 9 is found, *inter alia*, in the specification starting on page 9, line 6, to page 10, line 12, and FIG. 1. New claims 10-21 have been added. Support for new claims 10 and 18 is found, *inter alia*, in specification on page 12, lines 5-10, and page 14, lines 13-16. Support for new claims 11 and 16 is found, *inter alia*, in originally filed claim 6. Support for new claims 12, 17, and 21 is found, *inter alia*, in originally filed claim 7. Support for new claims 13 and 19 is found, *inter alia*, in originally filed claim 1 and in the specification starting on page 12, line 11, to page 13, line 20. Support for new claims 14 and 20 is found, *inter alia*, in originally filed claim 4 and in the specification on page 3, lines 10-16. Support for new claim 15 is found, *inter alia*, in originally filed claim 5. Applicants have amended the Summary of the Invention section so that it reflects the amendments to claims 1, 2, and 4-9, the cancellation of claim 3, and the addition of new claims 10 and 19. Also, applicants have amended the specification to correct for minor typographical and grammatical changes. Applicants have amended the Abstract of the Disclosure section so that it reflects new independent claim 19. No new matter has been added. Reexamination and reconsideration of the application, as amended, are respectfully requested.

On page 2 of the Office Action, the Examiner states: "The title of the invention is not descriptive. A new title is required that is clearly indicative of the invention to which the claims are directed." Applicants have amended the title of the invention to be clearly indicative of the invention to which the claims are directed.

Also, on page 2 of the Office Action, the Examiner objects to claims 5-7, "because of the following informalities: claim 5 recites 'has **such** a thickness'; claim 6 recites 'to **such** an extent'; claim 7 recites the expression 'or higher'." Applicants have amended claims 5, 6, and 7 to remove the informalities indicated by the Examiner. Therefore, applicants believe amended claims 5, 6, and 7 to be allowable. Withdrawal of these grounds for objection are respectfully requested.

On pages 2 and 3 of the Office Action, the Examiner rejects claims 3 and 4 under 35 U.S.C. § 112, second paragraph, as being indefinite. In particular, the Examiner states: "Claim 3 recites 'predetermined times'. Claim 4 recites 'predetermined thickness'. The expression 'predetermined' rendered the claims indefinite." Applicants have cancelled claim 3, and thus, the rejection to claim 3 is moot. Applicants respectfully traverse this rejection to claim 4. Applicants have amended claim 4 and removed the word "predetermined." Therefore, applicants submit that amended claim 4 complies fully with 35 U.S.C. § 112 and the rejection based thereon should be withdrawn.

On page 3 of the Office Action, the Examiner rejects claim 9 under 35 U.S.C. § 102(b) as being anticipated by Mori et al. (JP 06-080962). Anticipation requires that each and every element as set forth in the claims be found in a single prior art reference. *Verdegaal Bros., Inc. v. Union Oil Co. of California*, 814, F.2d 628, 631, 2 U.S.P.Q.2d (BNA) 1051, 1053 (Fed. Cir. 1987). Applicant respectfully traverses this rejection.

Claim 9 recites a semiconductor manufacturing apparatus including a reaction container, a heater, an object mounting device, a first gas charging port, and a second gas charging port. The heater is provided outside of the reaction container and the object mounting device is to be disposed in the reaction container. The first gas charging port is for charging bis tertiary butyl amino silane into the reaction container. The second gas charging port is for selectively charging one of  $\text{NH}_3$  and  $\text{NF}_3$ , thereby performing one of forming a silicon nitride film, by a thermal chemical vapor deposition method, on an object disposed in the reaction container,

with bis tertiary butyl amino silane and  $\text{NH}_3$  flowing into the reaction container, and removing silicon nitride formed in the reaction container with  $\text{NF}_3$  gas flowing into the reaction container.

Applicant submits that amended independent claim 9 is patentable over Mori because Mori does not teach or suggest each and every element as set forth in amended claim 9. Mori discusses a method for cleaning ammonium silicofluoride . However, Mori does not mention, “a heater provided outside of said reaction container; an object mounting device to be disposed in said reaction container; a first gas charging port for charging bis tertiary butyl amino silane into said reaction container; and a second gas charging port for selectively charging one of  $\text{NH}_3$  and  $\text{NF}_3$  . . . ,” and thus, does not teach or suggest each and every element as set forth in amended claim 9.

Accordingly, applicant submits that amended independent claim 9, and depending claims 13-18, are neither anticipated nor suggested by Mori, but rather is patentable over the cited reference.

On page 4 of the Office Action, the Examiner rejects claims 1-8 under 35 U.S.C. § 103(a) as being unpatentable over Mori in view of Moore et al. (USP 6,251,802). A prima facie obviousness rejection requires that the prior art reference, or references, when combined, must teach all of the claim limitations. MPEP § 2143.03; In re Fine, 837 F.2d 1071, 5 U.S. P.Q.2d (BNA) 1596 (Fed. Cir. 1988). Applicants have cancelled claim 3, and thus, the rejection to claim 3 is moot. Applicants respectfully traverse these rejections to claims 1, 2, and 4-8.

Claim 1 recites a semiconductor device manufacturing method including a first step of forming, by a thermal chemical vapor deposition method, a silicon nitride film on an object disposed in a reaction container, with bis tertiary butyl amino silane and  $\text{NH}_3$  flowing into the reaction container, and a second step of removing, without using plasma, silicon nitride formed in the reaction container, with  $\text{NF}_3$  gas flowing into the reaction container.

Claim 19 recites a reaction container cleaning method including flowing  $\text{NF}_3$  gas into the reaction container; and removing, without using plasma, a silicon nitride film formed in the reaction container.

Applicant submits that amended independent claim 1 and new independent claim 19 are patentable over Mori in combination with Moore because neither Mori nor Moore teach or suggest, “a second step of removing, without using plasma, silicon nitride formed in said reaction container, with  $\text{NF}_3$  gas flowing into said reaction container,” as required by claim 1, or, “flowing  $\text{NF}_3$  gas into the reaction container; and removing, without using plasma, a silicon nitride film formed in the reaction container,” as required by claim 19 (emphasis added). Mori merely mentions that after forming a silicon nitride film by a plasma CVD method using  $\text{SiH}_4$  and  $\text{NH}_3$ , plasma cleaning of the silicon nitride film is performed using  $\text{NF}_3$  gas. Thus, in Mori, a silicon nitride film is removed using a plasma. The Examiner, on page 4 of the Office Action, merely cites Moore because, “Moore et al. shows forming a silicon nitride layer with bis tertiary butyl amino silane and  $\text{NH}_3$  by chemical vapor deposition . . . .” Therefore, neither Mori nor Moore teach or suggest, “a second step of removing, without using plasma, silicon nitride formed in said reaction container, with  $\text{NF}_3$  gas flowing into said reaction container,” or, “flowing  $\text{NF}_3$  gas into the reaction container; and removing, without using plasma, a silicon nitride film formed in the reaction container.” (Emphasis added).

Accordingly, applicants submit neither Mori nor Moore, nor the combination of Mori and Moore, teach or suggest all of the requirements of amended independent claim 1 or new independent claim 19. Therefore, amended independent claim 1, new independent claim 19, and their depending claims 2, 4-8, 10-12, 20, and 21, are patentable over the cited references.

On page 5 of the Office Action, the Examiner rejects claims 1 under 35 U.S.C. § 103(a) as being unpatentable over Langan et al. (USP 5,413,670) in view of Moore. Applicants respectfully traverse this rejection.

Applicant submits that amended independent claim 1 and new independent claim 19 are patentable over Langan in combination with Moore because neither Langan nor Moore, as discussed above, teach or suggest, “a second step of removing, without using plasma, silicon nitride formed in said reaction container, with  $\text{NF}_3$  gas flowing into said reaction container,” as required by claim 1, or, “flowing  $\text{NF}_3$  gas into the reaction container; and removing, without using plasma, a silicon nitride film formed in the reaction container,” as required by claim 19 (emphasis added). Langan merely mentions that after forming a silicon nitride film using a plasma CVD reactor, plasma cleaning of the silicon nitride film is performed using  $\text{NF}_3$  gas. Thus, in Langan, silicon nitride film is removed using a plasma. Therefore, neither Langan nor Moore teach or suggest, “a second step of removing, without using plasma, silicon nitride formed in said reaction container, with  $\text{NF}_3$  gas flowing into said reaction container,” or, “flowing  $\text{NF}_3$  gas into the reaction container; and removing, without using plasma, a silicon nitride film formed in the reaction container.” (Emphasis added).

Accordingly, applicants submit neither Langan nor Moore, nor the combination of Langan and Moore, teach or suggest all of the requirements of amended independent claim 1 or new independent claim 19. Therefore, amended independent claim 1, new independent claim 19, and their depending claims 2, 4-8, 10-12, 20, and 21, are patentable over the cited references.

The art made of record but not relied upon by the Examiner has been considered. However, it is submitted that this art neither describes nor suggests the presently claimed invention, considered alone or in combination.

In view of the foregoing, it is respectfully submitted that the application is in condition for allowance. Reexamination and reconsideration of the application, as amended, are requested.

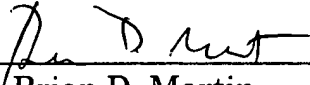
If for any reason the Examiner finds the application other than in condition for allowance, the Examiner is requested to call the undersigned attorney at the Los

Angeles, California telephone number (213) 337-6700 to discuss the steps necessary for placing the application in condition for allowance.

If there are any fees due in connection with the filing of this response, please charge the fees to our Deposit Account No. 50-1314.

Respectfully submitted,  
HOGAN & HARTSON L.L.P.

Date: June 20, 2002

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Version with markings to show changes made:

In the title:

SEMICONDUCTOR DEVICE MANUFACTURING METHOD AND  
[SEMICONDUCTOR MANUFACTURING ]APPARATUS FOR REMOVING  
SILICON NITRIDE FORMED IN A REACTION CONTAINER

In the specification:

Page 2, line 4, through page 6, line 13:

SUMMARY OF THE INVENTION

To solve the problems, the present inventors examined forming a silicon nitride ( $\text{Si}_3\text{N}_4$ ) film using  $\text{NH}_3$  and  $\text{SiH}_2(\text{NH}(\text{C}_4\text{H}_9))_2$  (bis tertiary butyl amino silane: BTBAS, hereinafter) as raw gases. As a result, the inventors have found that the silicon nitride film can be formed at a low temperature of about  $600^\circ\text{C}$  and  $\text{NH}_4\text{Cl}$ , which is a cause of metal contamination, is not generated.

However, the present inventors have found that the  $\text{Si}_3\text{N}_4$  film formed using BTBAS has the following drawbacks.

That is, BTBAS and  $\text{NH}_3$  introduced in a furnace are decomposed by heat, and the  $\text{Si}_3\text{N}_4$  film is formed not only on a wafer but also on an inner wall of a quartz reaction tube and an inner member made of quartz used in the reaction tube. The  $\text{Si}_3\text{N}_4$  film formed using BTBAS has a strong film stress and [a]the film shrinkage ratio is great. A  $\text{Si}_3\text{N}_4$  film formed by using DCS and  $\text{NH}_3$  and an  $\text{Si}_3\text{N}_4$  film formed by using BTBAS and  $\text{NH}_3$  were compared with each other. Comparison data of a film contraction ratio in percentage is shown in Fig.4, and comparison data of film stress is shown in Fig.5. In Figs.4 and 5, "B" shows an  $\text{Si}_3\text{N}_4$  film formed by using BTBAS and  $\text{NH}_3$ , and "D" shows an  $\text{Si}_3\text{N}_4$  film formed by using DCS and  $\text{NH}_3$ . The film stress means a tensile force (film stress), and the  $\text{Si}_3\text{N}_4$  film formed on a reaction furnace quartz comes off by the film stress. The film is shrunk by a high temperature (about  $600^\circ\text{C}$ ) of the reaction furnace. Since quartz does not

shrink or expand by heat and thus, distortion occurs. Therefore, when the  $\text{Si}_3\text{N}_4$  film becomes thick, a microcrack is generated, and particles are generated on the wafer. A thickness of an  $\text{Si}_3\text{N}_4$  film that may cause the microcrack is 4,000 Å.

To solve the problem of the particles, it is necessary to perform maintenance in such a manner that whenever a film thickness becomes 4,000 Å, a quartz inner tube 12, a quartz boat 14, and a quartz cap 15 of an vertical-type LPCVD (Low Pressure Chemical Vapor Deposition) film forming apparatus 1 are disassembled, and they are subjected to wet cleaning using HF (hydrogen fluoride) to remove the  $\text{Si}_3\text{N}_4$  film. When one time film forming operation forms a film of 1,000 Å thickness, it is necessary to perform the maintenance every four film forming operations. Further, there is a problem that it takes 16 hours to complete the maintenance, and this is too long.].

Thereupon, it is a main object of the present invention to solve the problem of high frequency of maintenance when an  $\text{Si}_3\text{N}_4$  film is produced using BTBAS and  $\text{NH}_3$ , and to provided a manufacturing method and a manufacturing apparatus of a silicon nitride film capable of reducing the maintenance frequency as small as possible and suppressing or preventing generation of particles.].

According to a first aspect of the present invention, there is provided a semiconductor device manufacturing method[, comprising] including:

a first step of forming, by a thermal chemical vapor deposition method, a silicon nitride film on an object disposed in a reaction container, with bis tertiary butyl amino silane and  $\text{NH}_3$  flowing into the reaction container, and

a second step of removing, without using plasma, silicon nitride formed in the reaction container, with  $\text{NF}_3$  gas flowing into the reaction container.

Preferably, the semiconductor device manufacturing method according to the first aspect of the present invention further comprises the first step after the second step. That is the semiconductor device manufacturing method according to the first



aspect of the present invention preferably comprises the first step, thereafter the second step and thereafter the first step again.

[Preferably, after repeating the first step predetermined times, the silicon nitride formed in the reaction container is removed, with  $\text{NF}_3$  gas flowing into the reaction container.

]Preferably, before the silicon nitride film formed in the reaction container [has]reaches a [predetermined ]thickness of  $4000 \text{ \AA}$ , the silicon nitride formed in the reaction container is removed, with  $\text{NF}_3$  gas flowing into the reaction container.

Preferably, before the silicon nitride film formed in the reaction container [has such ]reaches a thickness [as to generate]that generates particles on the object, the silicon nitride formed in the reaction container is removed, with  $\text{NF}_3$  gas flowing into the reaction container.

Preferably, the reaction container [itself ]is made of quartz and/or a member made of quartz is used in the reaction container, and before [a thickness of ]the silicon nitride film formed on the quartz is increased to [such an extent as to generate]a thickness that generates particles on the object, the  $\text{NF}_3$  gas is allowed to flow into the reaction container to remove the silicon nitride formed on the quartz. In this case, it is preferable to remove the silicon nitride with  $\text{NF}_3$  gas before the thickness of the silicon nitride becomes  $4000 \text{ \AA}$  or larger.

Preferably, the second step is carried out in a state where a pressure in the reaction container is [set]greater than or equal to 10 Torr[ or higher].

Preferably, the semiconductor device manufacturing method according to the first aspect of the present invention further comprises a step of purging the reaction container using the  $\text{NH}_3$  gas at least one of before and after the first step.

Preferably, every time a thickness of the formed silicon nitride film reaches  $3000 \text{ \AA}$ , the silicon nitride film formed in the reaction container is removed, with  $\text{NF}_3$  gas flowing into the reaction container.

According to a second aspect of the present invention there is provided a semiconductor manufacturing apparatus [comprising]including:

a reaction container[, wherein];  
a heater provided outside of the reaction container;  
an object mounting device to be disposed in the reaction container;  
a first gas charging port for charging bis tertiary butyl amino silane into the reaction container; and  
a second gas charging port for selectively charging one of  $\text{NH}_3$  and  $\text{NF}_3$ , thereby performing one of

forming a silicon nitride film[ is formed], by a thermal chemical vapor deposition method, on an object disposed in the reaction container, with bis tertiary butyl amino silane and  $\text{NH}_3$  flowing into the reaction container, and  
removing silicon nitride formed in the reaction container[ is removed], with  $\text{NF}_3$  gas flowing into the reaction container.

According to third aspect of the present invention there is provided a reaction container cleaning method including:

flowing  $\text{NF}_3$  gas into the reaction container; and  
removing, without using plasma, a silicon nitride film formed in the reaction container.

Page 20, lines 1-9:

#### ABSTRACT

A [semiconductor device manufacturing]reaction container cleaning method [comprises a first step of forming, by a thermal chemical vapor deposition method, a silicon nitride film on an object disposed in a reaction container, with bis tertiary butyl amino silane and  $\text{NH}_3$  flowing into the reaction container, and a second step of

removing silicon nitride formed in the reaction container, with  $\text{NF}_3$  gas flowing into]includes flowing  $\text{NF}_3$  gas into the reaction container, and removing, without using plasma, a silicon nitride film formed in the reaction container.

**In the claims:**

1. (Amended) A semiconductor device manufacturing method[,] comprising:  
a first step of forming, by a thermal chemical vapor deposition method, a silicon nitride film on an object disposed in a reaction container, with bis tertiary butyl amino silane and  $\text{NH}_3$  flowing into [the]said reaction container, and  
a second step of removing, without using plasma, silicon nitride formed in said reaction container, with  $\text{NF}_3$  gas flowing into said reaction container.
2. (Amended) [A]The semiconductor device manufacturing method as recited in [Claim]claim 1, further comprising said first step after said second step.
4. (Amended) [A]The semiconductor device manufacturing method as recited in [Claim]claim 1, wherein  
before said silicon nitride film formed in said reaction container [has]reaches a [predetermined ]thickness of 4,000 Å, said silicon nitride formed in said reaction container is removed, with said  $\text{NF}_3$  gas flowing into said reaction container.
5. (Amended) [A]The semiconductor manufacturing method as recited in [Claim]claim 1, wherein  
before said silicon nitride film formed in said reaction container [has such]reaches a thickness [as to generate]that generates particles on said object, said silicon nitride formed in said reaction container is removed, with said  $\text{NF}_3$  gas flowing into said reaction container.

6. (Amended) [A]The semiconductor device manufacturing method as recited in claim 1, wherein

said reaction container [itself] is made of quartz [and/or] and a member made of quartz is used in said reaction container, and

before [a thickness of] said silicon nitride film formed on said quartz is increased to [such an extent as to generate] a thickness that generates particles on said object, said  $\text{NF}_3$  gas is allowed to flow into said reaction container to remove said silicon nitride formed on said quartz.

7. (Amended) [A]The semiconductor device manufacturing method as recited in claim 6, wherein

said second step is carried out in a state where a pressure in said reaction container is [set] greater than or equal to 10 Torr[ or higher].

8. (Amended) [A]The semiconductor device manufacturing method as recited in claim 1, further comprising a step of purging said reaction container using said  $\text{NH}_3$  gas at least one of before and after said first step.

9. (Amended) A semiconductor manufacturing apparatus comprising:  
\_\_\_\_\_ a reaction container[, wherein];

a heater provided outside of said reaction container;

an object mounting device to be disposed in said reaction container;

a first gas charging port for charging bis tertiary butyl amino silane into said reaction container; and

a second gas charging port for selectively charging one of  $\text{NH}_3$  and  $\text{NF}_3$ ,  
thereby performing one of

forming a silicon nitride film[ is formed], by a thermal chemical vapor deposition method, on an object disposed in said reaction container, with bis tertiary butyl amino silane and  $\text{NH}_3$  flowing into [the]said reaction container, and

removing silicon nitride formed in said reaction container[ is removed,] with  
NF<sub>3</sub> gas flowing into said reaction container.